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Supplementary Material

A peptide-based supercapacitor and its performance improvement via TiO2 coating

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1. Materials and Methods

The Fmoc-EF-NH_2 (Chinapeptide Co., China), polyvinyl alcohol (PVA, Aladdin Co., China), H_3PO_4, PET plate (0.1 cm), and reagents were purchased from HualiDe Ltd. All chemical reagents are in analytical grade.

2. Preparation of SC devices

The preparation of PVA/H_3PO_4 electrolyte was performed as follows: 3 g of PVA was dispersed into 30 mL of deionized water, and then heated to 85 °C under continually stirring until clear solution was obtained. In the cooling-down process, the concentrated 10 mL of analytical reagent H_3PO_4 was dropped into the viscous solution under sufficiently stirring until a clear solution was obtained. The sandwich structure devices of peptide capacitor were assembled in the following way: A large PET substrate was coated with 20 nm Au film by using dc magnetron sputtering, and it was then cut into small regular pieces. The peptide films of different thicknesses were prepared by drop casting of dispersed peptide nanofibers in water on these regular Au-coated PET pieces, and after drying for removal of water, the copper tapes were adhered by silver plastic to one edge of each Au-coated PET piece. The PVA/H_3PO_4 electrolyte was then spread onto the peptide films, and after drying for removal of excess water, two pieces of Au-coated PETs were pressed together to form a classical sandwich structure device.

3. Atomic layer deposition (ALD)

The Fmoc-EF-NH_2 was dissolved in ddH_2O water to form a peptide organogel via sonication. The peptide nanonetwork template was simply fabricated by evaporating water, which was followed by the deposition of a 20 nm layer of TiO_2 on the obtained peptide template via ALD under 3 Torr at 80 °C. TiO_2 ALD films were grown directly on graphene using a rotary ALD reactor.[1-3] For the TiO_2 ALD, the titanium tetrachloride (TiCl4, 99.8%, J&k Chemicals) and high-performance liquid chromatography (HPLC) grade H_2O reactants were obtained from Sigma-Aldrich. The typical growth rate for the TiO_2 ALD chemistry is ~0.6 Å per cycle. The TiO_2 ALD reaction sequence was: i) TiCl4 dose to 1.0 Torr; ii) evacuation of reaction products and excess TiCl4; iii) H_2O dose to 1.0 Torr, iv) evacuation of reaction products and excess H_2O. The TiO_2 ALD was conducted at 80 °C. 330 ALD cycles were repeated to obtain a TiO_2 thickness of 20 nm.

4. Characterization

The XRD patterns were collected on SmartLab with Cu Kα radiation (λ = 1.5406 Å, Rigaku,

Japan). The SEM image was taken using a scanning electron microscope (S-4800, Hitachi, Japan). The Raman measurement was carried out on a Renishaw inVia micro-Raman spectroscopy with a laser radiation of 532 nm. In order to characterize the peptide assemblies, the peptide nanofiber dispersion was dropped onto holey carbon support film with 200 mesh copper grids. The TEM images and SAED of the peptide nanofibers were obtained using a transmission electron microscope (JEM-2010, JEOL, Japan). The electrochemical measurements were carried out on CHI-660E electrochemical workstation (China, Shanghai). The CV and charging/discharging techniques were employed to investigate electrochemical performance of electrodes.

5. Calculations

The capacitance values of the device were calculated[4-6] according to the CV curves as following Equation (1):

$$\mathrm{Cs} = \frac{\int i(V)dV}{2Sv\Delta V}$$

The capacitance values of the device were calculated from the charging/discharging curves as following Equation (2):

$$\mathrm{Cs} = \frac{I\Delta t}{S\Delta V}$$

where C_S refers to areal capacitance of the device; S (cm^2) is the area of the electrodes; v is the potential scan rate (V S^{-1}); ΔV is the potential window (V); and Δt is the discharging time (s).

Supplementary Figures

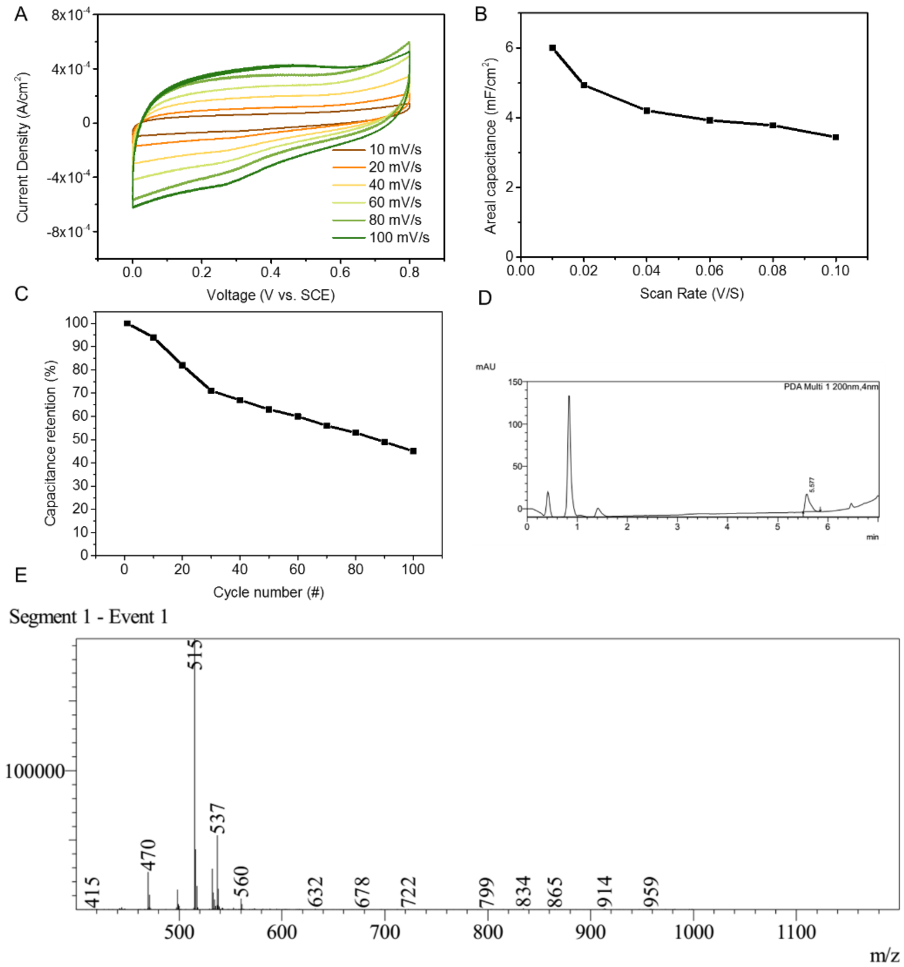

Figure S1. (A) CV curves of the peptide electrode at different scan rates. (B) Plots of Scan rates against the areal capacitance. (C) Cycling performance of the peptide electrodes collected at a scan rate of 100 mV/s for 100 cycles. (D) HPLC elution curve for electrolyte. (E) Mass spectrum for FE-Fmoc. The detector was in negative ion mode. (FE-Fmoc, $M/Z_{cal.}$=516, M/Z_{obs}=515).

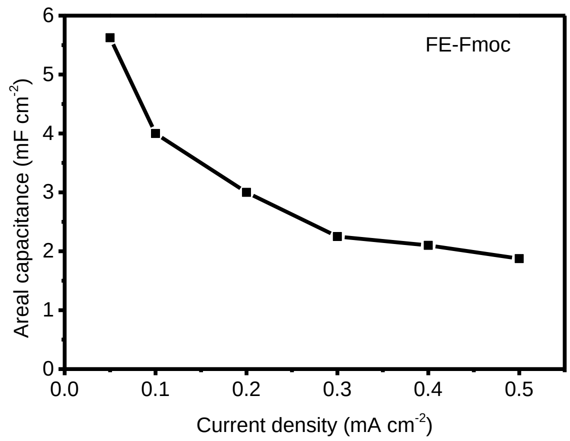

Figure S2. Summary plot of areal capacitance versus different current densities for the all solid-state peptide//peptide device.

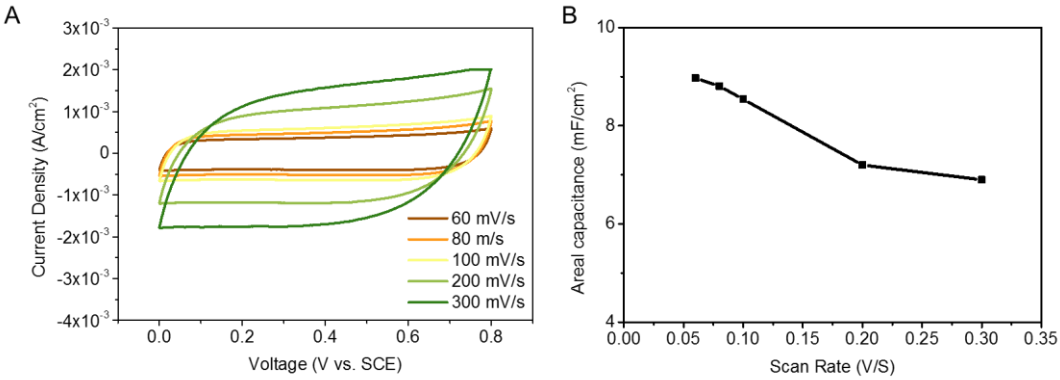

Figure S3. (A) CV curves of the peptide@TiO_2 electrode at different scan rates. (B) Plots of Scan rates against the areal capacitance.

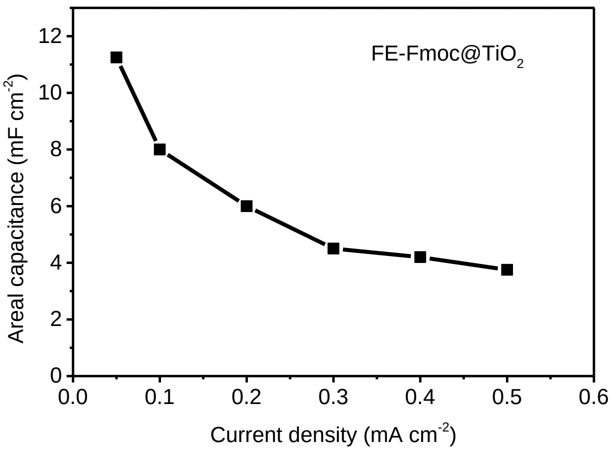

Figure S4. Summary plot of areal capacitance versus different current densities for the all-solid- state peptide@TiO_2//peptide@TiO_2 device.

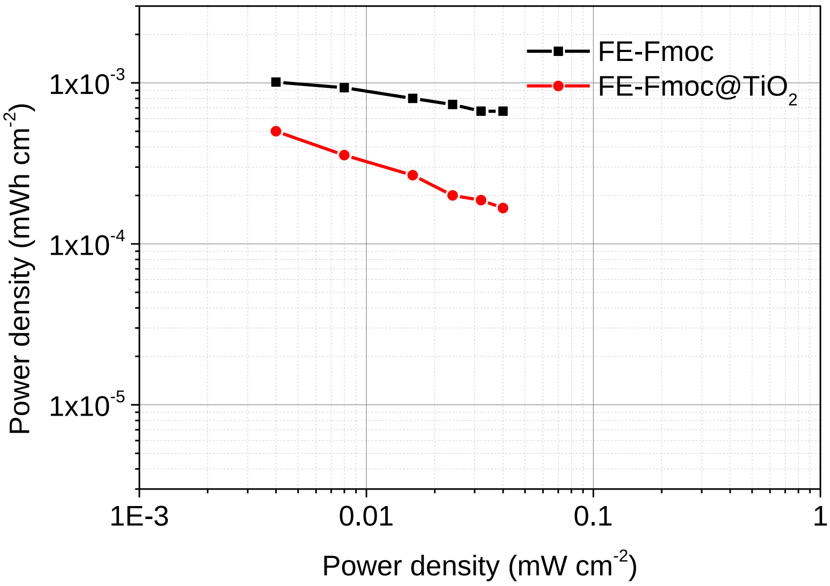

Figure S5. Ragone plots of FE-Fmoc peptide device and FE-Fmoc@TiO_2 device.

Table S1. Comparison of areal capacitance in this study with reported peptide-based electrodes.

No.	Flexible electrode materials	Areal capacitance for electrode (mF cm^{-2})	Areal capacitance for supercapacitor (mF cm^{-2})	Reference
1	FF dipeptides nanotubes	0.48-0.58 (100 mV s^{-1})	-	*Ref. 7*
2	FF dipeptides nanotubes	0.16-0.24	-	*Ref.8*
3	FF dipeptides nanotubes	0.8 (100 mV s^{-1})	-	*Ref. 9*
4	FF dipeptides nanotubes	1 (50 mV s^{-1})	-	*Ref. 10*
5	FE-Fmoc	3.443 (100 mV s^{-1})	2.5 (100 mV/s)	*this article*
6	FE-Fmoc@TiO2	8.541 (100 mV s^{-1})	5.8 (100 mV/s)	*this article*

Table S2. Comparison of the devices' areal capacitance, energy density, and power density in this study with other reported flexible all-solid-state supercapacitors.

NO.	Flexible electrode materials	Areal capacitance for supercapacitor (mF cm^{-2})	Areal power density (mW cm^{-2})	Areal energy density (mW h cm^{-2})	Reference
1	PANI/GO	25.7 (5 mV/s)	0.01	0.00252	*Ref. 11*
2	PANI	51.7 (0.1 mA/cm^2)	-	-	*Ref. 12*
3	CNT-GO/Ppy	70 (10 mV/cm^2)	3.7	0.0063	*Ref. 13*

4	GO/Ppy	387.7 (0.2 mA/cm^2)	0.08	0.0168	*Ref. 14*
5	Ppy/GO	152 (10 mV/s)	0.954	0.0129	*Ref. 15*
6	TiO2/Ppy	64.5 (10 mV/s)	-	-	*Ref. 16*
7	GO/PANI	355.5 (0.5 mA/cm^2)	-	-	*Ref. 17*
8	GO/PEDOT-CNTs	33.4 (10 mV/s)	4	0.0044	*Ref. 18*
9	carbon paper/Ppy	13.42 (50 mV/s)	3.47	0.00061	*Ref. 19*
10	FE-Fmoc	10.5 (0.1 mA/s)	0.02	0.0005	this article
11	FE-Fmoc@TiO2	4 (0.2 mA/s)	0.02	0.001	this article

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